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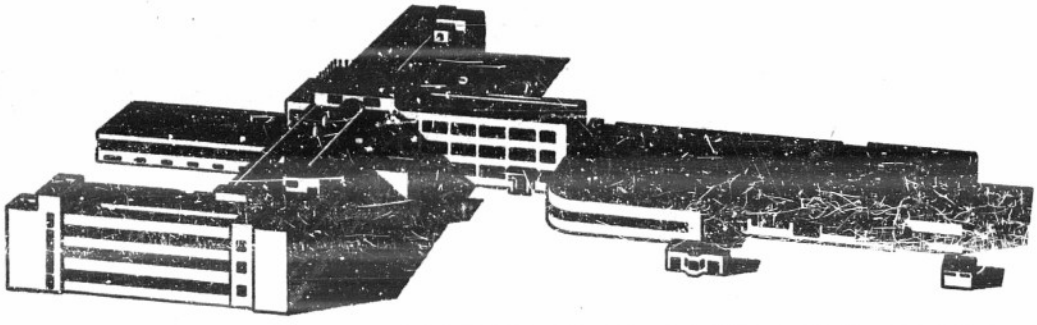

DAVID SARNOFF RESEARCH CENTER
PRINCETON, NEW JERSEY

SIXTEENTH INTERIM REPORT

INFRARED PHOTOCONDUCTORS

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I. Introduction

The best photoconductive material developed so far during the course of the project being reported is gold-arsenic doped germanium. This material shows photoconductive response in the far infrared region when cooled to liquid nitrogen temperature. Its spectral response which, in addition to the intrinsic germanium peak, has a broad impurity response with a maximum at 6 or 7 microns and extending to beyond 10 microns has been described in earlier reports.

The work during the pericd covered by this report was divided between a study of the gold-arsenic-germanium system and the examination of germanium doped with other impurities.

The problems remaining in connection with the gold-arsenic-germanium system are a better understanding of the energy level system which is responsible for its good response characteristics, an investigation to determine whether the impurity concentration, and consequently the absorption coefficient of the material, can be increased, and the optimum method of utilization of the material. In connection with the problem of the energy level structure, the following two aspects must be studied in some detail.

(1) Whether the log conductivity versus 1/T slope of about .05 ev consistently found in these Laboratories when germanium is doped with high purity gold is really characteristic of the gold-only doped germanium; and

(2) Why various samples of gold-arsenic doped germanium exhibit such a wide range of log conductivity versus 1/T slopes. Values ranging between .08 and .18 ev have been observed. No corresponding variation in the photoconductivity threshold or in the shape of the impurity photoconductive response appears to exist.

The study of other impurity dopings was aimed at determining whether a material could be found that has a slightly longer wavelength response than the gold-arsenic photoconductor but still can be used at liquid nitrogen temperature and/or a material which is capable of supporting a higher impurity concentration. The impurities being studied are those located two or more columns on either side of germanium in the Periodic Table; in particular, germanium doped with zinc and arsenic, silver, silver and antimony, copper and antimony, and chromium were studied.

II. Study of Doped Germanium

A. Gold-Arsenic Doped Germanium

1. Effects of Surface Treatment

One possible reason for the spread in log conductivity versus 1/T slopes observed for gold-arsenic doped germanium might be differences in the state of the surface of various samples in spite of the fact that the mounting techniques have been kept as reproducible as possible from sample to sample. In order to check this possibility, a previously measured sample, AA230, which had given an abnormally small slope, 0.10 ev., was subjected to several different etching treatments under conditions such that the contact areas of the sample were protected from attack. After each treatment, the conductance of the sample was determined at room temperature; at liquid nitrogen temperature; and at the temperature of maximum conductance. For five different etch treatments, the average deviation from the average of the ratio of the maximum conductivity to the room temperature conductivity was 2.5 percent. For the ratio of the maximum conductivity to the liquid nitrogen temperature conductivity, the average deviation from the average was 17 percent. A change of 17 percent in the magnitude of this ratio would produce a change of about 5 percent in the magnitude of the slope of the log conductivity versus 1/T curve. A detailed measurement of the temperature dependence of conductivity of the sample after the sequence of etch treatments was completed gave a value of the slope which agreed with the original value within 10 percent. Evidently, the effects due to differences

in surface treatment of the samples are too small to account for the spread in the magnitude of the slopes of gold-arsenic doped samples which has been observed.

2. Effects of Polycrystallinity

In order to investigate the effect of polycrystallinity upon the behavior of gold-arsenic doped germanium, a portion of crystal 350L which was p-type with a resistivity of about 2 ohm cm and which showed the characteristic steep conductivity slope was melted and then rapidly cooled to form a polycrystalline button. Two bars, AA267 from near the surface and AA268 from the interior of the button, were cut from this material and tested over the range from room temperature to liquid nitrogen temperature. Although both samples were p-type, their room temperature resistivities were 15 ohm cm for AA267 and 40 ohm cm for AA268. Both samples showed an intrinsic drop upon cooling from room temperature but neither showed the steep impurity slope characteristic of the starting material. From this observation, it may be concluded that the gold-arsenic doped germanium must be prepared as single crystals in order to obtain the desired properties.

B. Zinc-Arsenic Doped Germanium

One crystal (354L) doped with zinc and stepwise with arsenic has been studied in the search for an impurity level lying at a higher energy than the 0.03 ev level characteristic of zinc only. Seven samples were measured in the Collins Cryostat. One of these, AA242 was cut from the zinc-only section; three, AA243-245, were cut from the next section containing a small

concentration of As and the remaining samples AA247-249 were cut from a third section containing a larger As concentration. The behavior of these samples is summarized in Table I. Log conductivity versus inverse absolute temperature curves for some of

TABLE I

Zinc-Arsenic Doped Germanium

Sample Number	Conductivity Type	Rm. Temp. Resistivity	Low Temp. Slope	Photoconductance at 4°K *
AA242	p	10 ohm cm	0.035 ev	2.0×10^{-1} μA/volt
AA243	p	35	0.044	1.3×10^{-3}
AA244	mixed	(57)	0.3	1×10^{-5}
AA245	n	(79)	0.3	2×10^{-6}
AA247	n	19	0.014	6.0×10^{-3}
AA248	n	29	0.23	1.3×10^{-4}
AA249	n	14	0.015	5.7×10^{-2}

*Response to room temperature radiation.

these samples are plotted in Fig. 1. The behavior of the sample from the zinc-only section was typical of zinc-doped germanium. In the first arsenic-zinc doped section, a transition from p- to n-type conductivity occurred. The second arsenic-zinc doped section was predominantly n-type. The samples from this section, except for AA248, show behavior more or less typical of arsenic doped germanium. The behavior of AA248 is not understood at present. The results for this system do not indicate the presence

of acceptor levels lying deeper that about 0.03 ev. These results, however, are incomplete since there were no p-type samples containing both arsenic and zinc impurities having resistivities less than 35 ohm cm. The system is rather difficult to work with due to the considerable volatility of zinc at the melting point of germanium.

C. Silver Doped Germanium

In the past two attempts at growing silver-doped germanium crystals had been made. The behavior of samples cut from each of these crystals was difficult to understand and probably represented the effects of extraneous residual impurities. During the present period, one more silver-doped crystal (355L) was grown. Great care was exercised in this attempt to minimize the effects of residual impurities. The behavior of samples from this crystal are believed to be typical of silver (possibly with a balancing impurity) doped germanium. The samples are p-type and exhibit low temperature log conductance versus inverse absolute temperature slopes of about 0.17 ev. One example of the type of curve observed is illustrated in Fig. 2. From the fact that although the melt from which the crystal was grown contained a high concentration of silver (about 0.4 weight percent), the samples measured showed an intrinsic drop upon cooling from room temperature, it may be concluded that the limiting solubility of silver in germanium is small and of the order of magnitude of about 10^{13} cm^{-3}. The difference in the solubility of silver as compared with that of copper or gold in germanium is striking.

Nevertheless, a sample of this material has shown photoconductivity at liquid nitrogen temperature extending out to about 8 microns. This would indicate that there is reasonable agreement between the optical and thermal activation energies in this case.

D. Silver-Antimony Doped Germanium

In view of the low solubility of silver in germanium, a search for possible multiple levels would be very difficult. Nevertheless, one attempt to grow a silver-antimony crystal was made. Unfortunately, this attempt resulted in a polycrystalline ingot rather than a single crystal. No useful information was obtained from an examination of samples cut from the ingot.

E. Copper-Antimony Doped Germanium

Two crystals, 361L and 362L, doped with copper and antimony were grown and studied during this period in the search for a level due to copper lying at a larger energy than 0.04 ev. Both crystals contained first a copper-only section followed by two sections containing copper and antimony in different relative concentrations. In crystal 361L, both lower sections were n-type. This indicates that too much antimony had been added.

Smaller amounts of antimony were added in the growth of 362L. The copper-only section was p-type and included the room temperature resistivity range from 1.7 ohm cm at the top to 0.7 ohm cm near the bottom. The first copper-antimony double-doped section was also p-type throughout and included the resistivity range from 0.8 ohm cm to 11 ohm cm. However, the resistivity

was not a smooth function of distance along the crystal. This indicates that there was inadequate mixing of the melt after addition of the antimony. Of the eight samples cut from this section of the crystal, four had room temperature resistivities in the range from 6 to 11 ohm cm. Each of these four samples had a considerably higher resistivity at liquid nitrogen temperature than at room temperature. The temperature dependence of conductivity of two of these samples has been measured in detail. The results are presented in Figs. 3 and 4. The behavior of the two samples is distinctly different. AA280 which was measured between 410°K and 140°K was intrinsic only above about 350°K. Below about 180°K, the log conductivity versus 1/T curve is approximately linear with a slope of about 0.4 ev. The other sample, AA287, which actually had a lower room temperature resistivity than AA280, was in the intrinsic range already at room temperature. At lower temperatures, the log conductivity versus 1/T curve showed two linear portions with slopes of 0.06 and 0.045 ev. Neither the behavior of AA280 or of AA287 is characteristic of copper-only doped germanium. Whether either of these samples can be considered to furnish evidence for the existence of a second level due to copper is still uncertain since, as indicated above, the section of the crystal from which these samples were cut was not particularly homogeneous.

F. Chromium Doped Germanium

One sample of chromium doped germanium cut from a crystal grown by another group has been measured to low temperatures. The

slope of the log conductance versus 1/T curve was found to be 0.029 ev. Chromium might be expected to be a multi-level impurity in germanium and, therefore, further work with this impurity might be of interest.

G. Gold Doped Germanium

Germanium doped with high purity gold only has been found to exhibit a log conductivity versus 1/T slope of about 0.05 ev at low temperatures. The curves also usually show double conductivity maxima at about 250°K and 90°K. This behavior has apparently not been found by others working with gold doped germanium.

In an attempt to determine whether or not this behavior might in some manner be due to a non-uniform distribution of impurity along a diameter of the grown crystal, a previously measured sample was cut in a manner such as to provide one bar from along the axis of the crystal and a parallel bar from near the surface. The conductances of the two samples were observed as function of the temperature between room temperature and liquid nitrogen temperature. No essential difference in the behavior of the two samples was found. It may be concluded, therefore, that the observed characteristics of gold-only doped samples are not due to a gross impurity concentration gradient across the crystal.

III. Spectral Response Measurements

A. Germanium

The initial purpose of the measurements to be described was to check whether the 6 - 10 micron response of gold doped germanium balanced with arsenic is a result of the arsenic balancing one set of the gold levels, as has been discussed previously in these reports, or whether this response is found "intrinsically" in germanium whenever balancing impurities are present. For this purpose, measurements of the response in the infrared of AA259 at liquid nitrogen temperature were made. This crystal was cut from a low antimony doped crystal in a region where the antimony was apparently balanced by residual impurities since the resistivity at room temperature was intrinsic and, on cooling, the conductivity initially fell intrinsically. At liquid nitrogen temperature, the intrinsic response was extremely high but no real response in the 4 to 15 micron region was found.

Measurements of several transistor junctions in the back direction at liquid nitrogen temperature also showed no response in this region.

These results indicate that the 6 - 10 micron response of gold-arsenic-germanium is a direct result of the gold-arsenic impurity content of the germanium.

Because of the extremely high sensitivity of the cooled AA259 crystal in the intrinsic region, some short wavelength scattered light around the six micron setting of the Leiss system was detected. In fact, the "response" measured in this

region was identical to that measured for the zinc-arsenic-germanium crystals from 354L as described in the last report. This undoubtedly means that response was spurious and that zinc-arsenic-germanium, which has an activation energy of 0.03 ev, photoconducts only beyond 15 microns. The scattering, it must be noted, is relatively weak and does not affect our previous measurements of gold-arsenic-germanium which has a definite response out to 10 - 12 microns.

The spectral response of AA256, silver-doped germanium at liquid nitrogen temperature exhibited weak response out to 8 microns. The response was slightly obscured in part by the scattering discussed above. Neighboring crystals showed activation energies of 0.14 and 0.17 ev with short intrinsic drops on cooling indicating low silver content.

B. Miscellaneous

Spectral response measurements for this and other laboratory groups were made on lead sulfide, lead telluride, potassium antimonide and cesium antimonide films at room and liquid nitrogen temperatures.

IV. Preparation of Germanium Crystals

After the crystal growing equipment had been moved to the radiochemistry laboratory it was found that vibrations due to a heavy blower mounted just outside the room interfered with the growth of single crystal material. This difficulty was eliminated by mounting the entire table which carried the crystal growing equipment upon Lord mounts.

A list of the crystals grown during this period follows.

355L - 10g Ge and 37 mg of Johnson and Matthey silver.

356L - Pure Ge grown for seeds.

357L - 9.7 g Ge plus a 0.5 g piece upon which had been electroplated approximately 40 micrograms of Sb.

358L - 11.4 g of Ge plus 150 mg of Johnson and Matthey Sb. The melt was rapidly cooled to form a polycrystalline button. This material was prepared to be used in the doping of other crystals with Sb.

359L - 10 g of Ge plus 100 mg of Johnson and Matthey silver. After one-third of the crystal was grown, 12 mg of 358L (Ge:Sb) were added. After approximately one-fourth more of the crystal was grown, 6.7 mg of Johnson and Matthey antimony was added. The growth of the crystal was then completed.

360L - 2.0 g of 350L (Ge:Au-As) melted and rapidly cooled to form a polycrystalline button.

361L - 10.2 g of Ge plus 10 mg of Johnson and Matthey Cu. After one-fourth of the crystal was grown, 12.8 mg of 358L (Ge:Sb) were added. After one-third more was grown, 80 mg

of 358L (Ge:Sb) were added. Then, growth was completed.

362L - 11 g of Ge plus 16 mg of Johnson and Matthey Cu. After about 2.5 g of Ge were drawn, 7 mg of 358L (Ge:Sb) were added. After 2.3 g more were drawn, 12 mg of 358L (Ge:Sb) were added and the crystal drawn to completion.

V. Equipment

A. Infrared Detector, Type AA

The final design of this cell, described in the previous report, is incomplete pending further exploratory experiments concerning the type of cell shielding required for maximum efficiency.

B. Far Infrared

The inability of the model shop to obtain vacuum tight soldered joints has resulted in a temporary suspension of the construction of the dewar for Ohio State University Research Foundation.

C. Optical and Electrical

The angle iron table for the Leiss monochromator system and associated electrical system was completed during this period and the whole system is now in operating condition.

VI. Miscellaneous

A. Special Cells

1. Low Temperature Cells for N.R.L.

In a recent visit, Berhens and Mears from N.R.L. discussed the possibility of obtaining from us several large disc-type samples of arsenic or indium doped germanium for use as an infrared detector at liquid helium temperatures. These samples are to be mounted by RCA in holders which fit into their dewar. At present we are awaiting receipt of their holders.

2. Alloyed Gold-Arsenic-Germanium Junctions

Six alloyed junctions of gold on arsenic doped germanium were prepared by Tube Assembly. It was hoped to achieve a gold-arsenic balance region in this way so that the available techniques of tube assembly can be used for producing balanced infrared detectors. No sensitivity in the 6 - 10 micron region was found on cooling these junctions to liquid nitrogen temperature so that opparently insufficient gold entered the germanium to balance the arsenic already present because of the low solubility limit of gold.

Six more junctions were prepared in which antimony-rich lead was alloyed to gold doped germanium. These junctions showed some very weak response beyond the intrinsic region when cooled to liquid nitrogen temperatures. The alloyed junction comprised a dot of the antimony-lead on the germanium. It is proposed to make more of this type of junction using, however, a broader area junction.

B. Other Measurements

Attempts were made to achieve breakdown in crystal AA232, gold-aresenic-germanium, at liquid nitrogen temperature similar to the low temperature breakdown observed for arsenic-doped germanium at 4°K. Measurements of current were made for fields up to 1000 volts/cm. Beyond 600 volts/cm extreme non-linearity was observed; it is not known yet whether this was a true breakdown.

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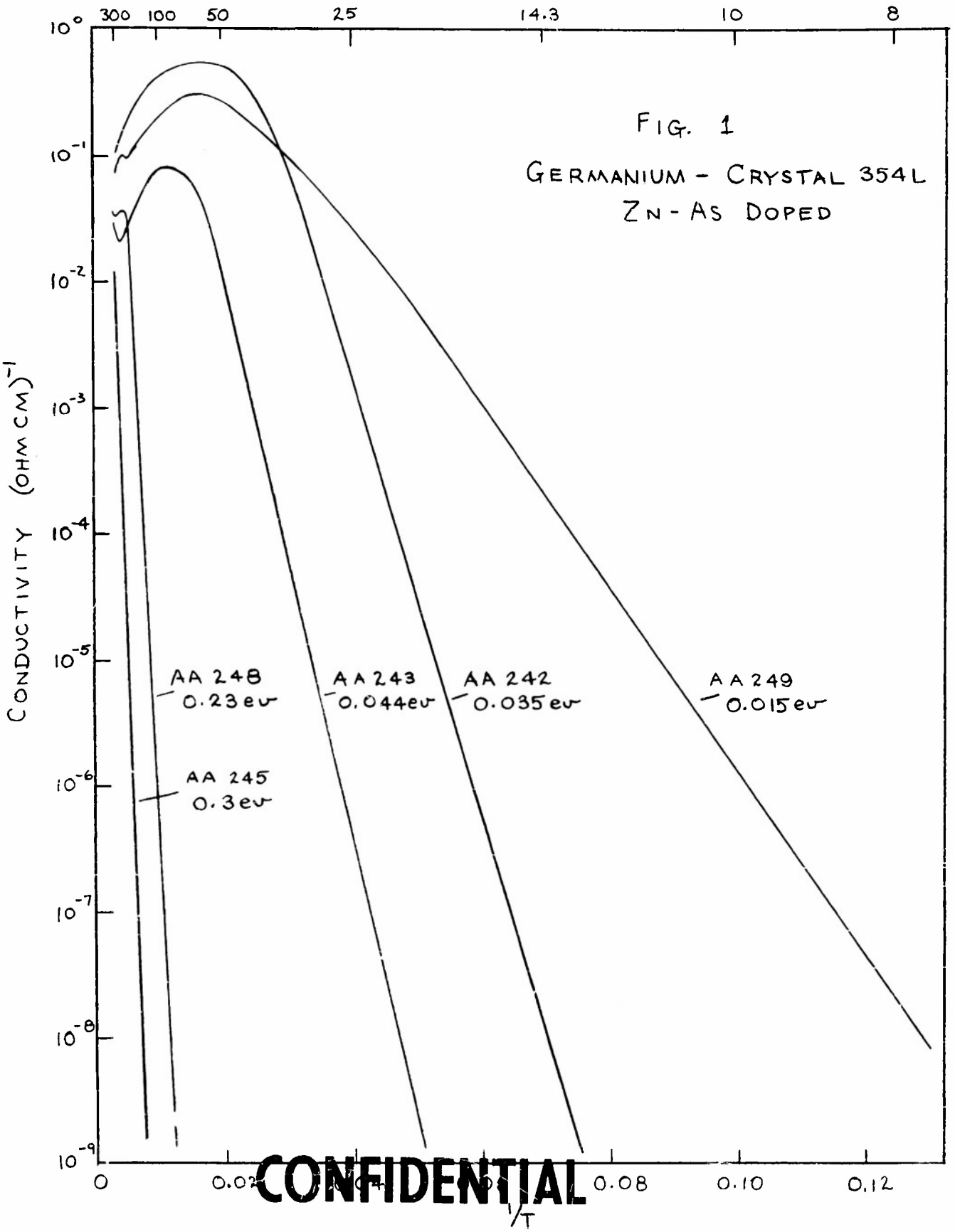


FIG. 1

GERMANIUM - CRYSTAL 354L

ZN - AS DOPED

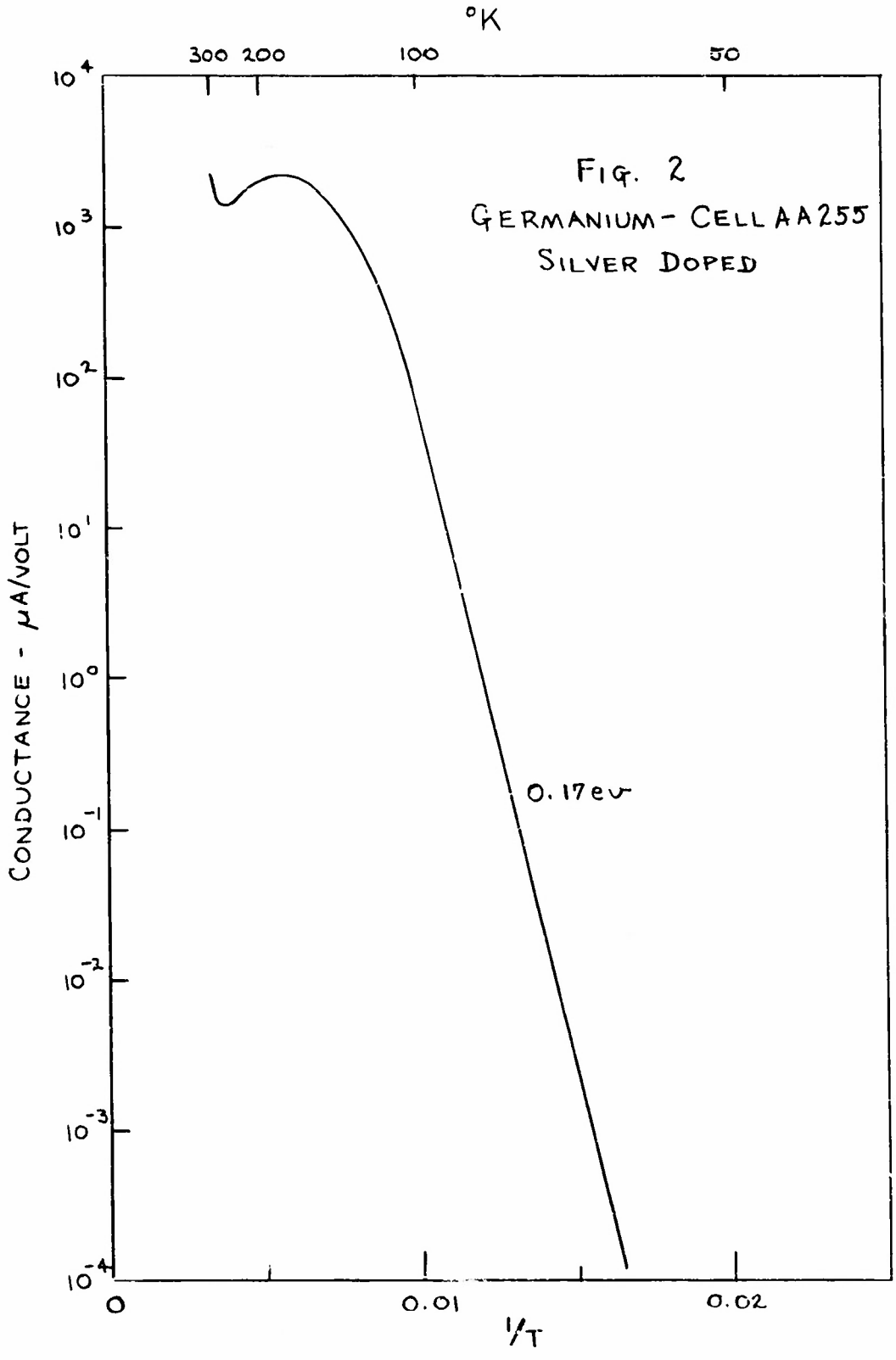
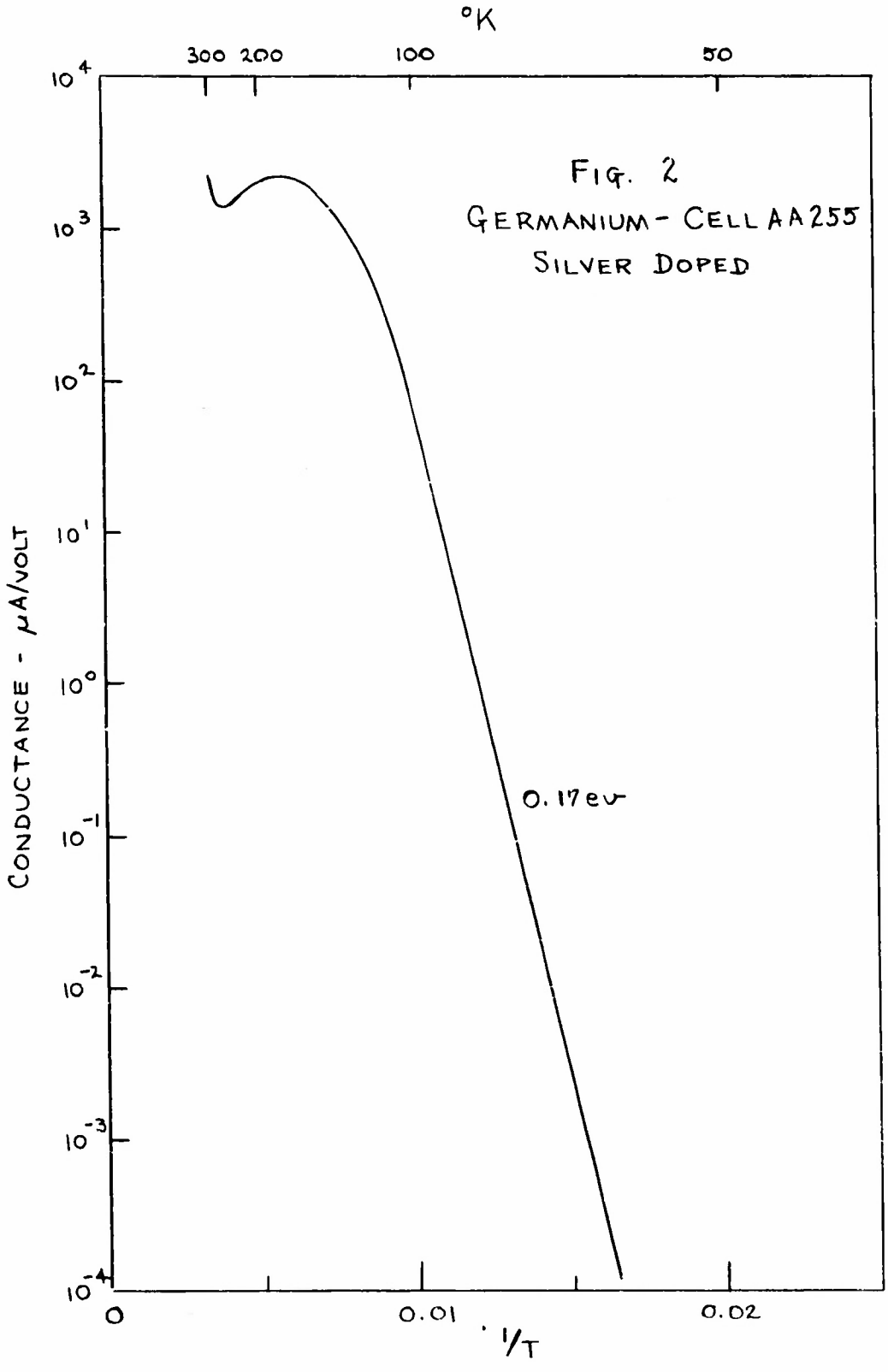


FIG. 2
GERMANIUM - CELL AA255
SILVER DOPED



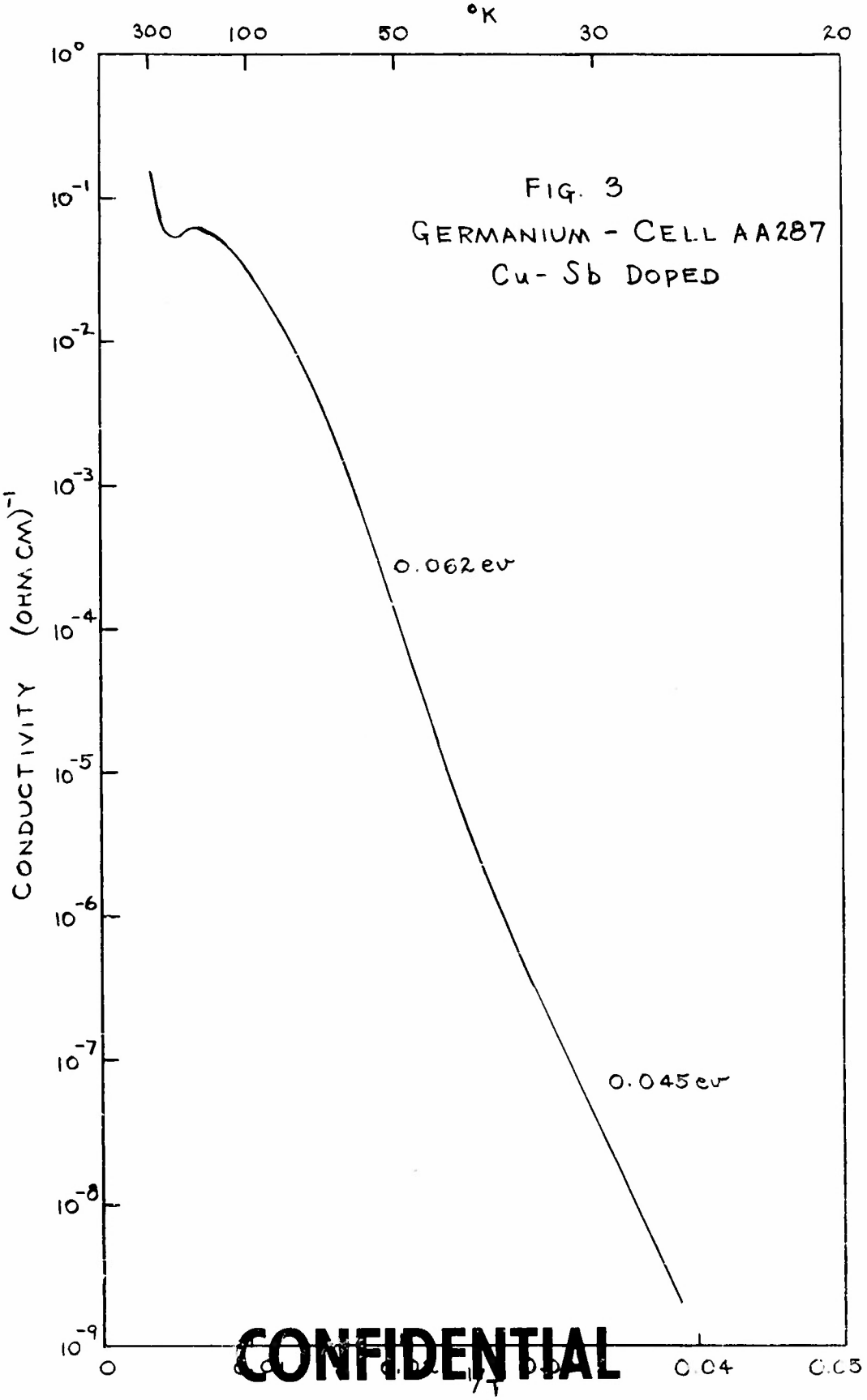


FIG. 3
GERMANIUM - CELL AA287
Cu - Sb DOPED

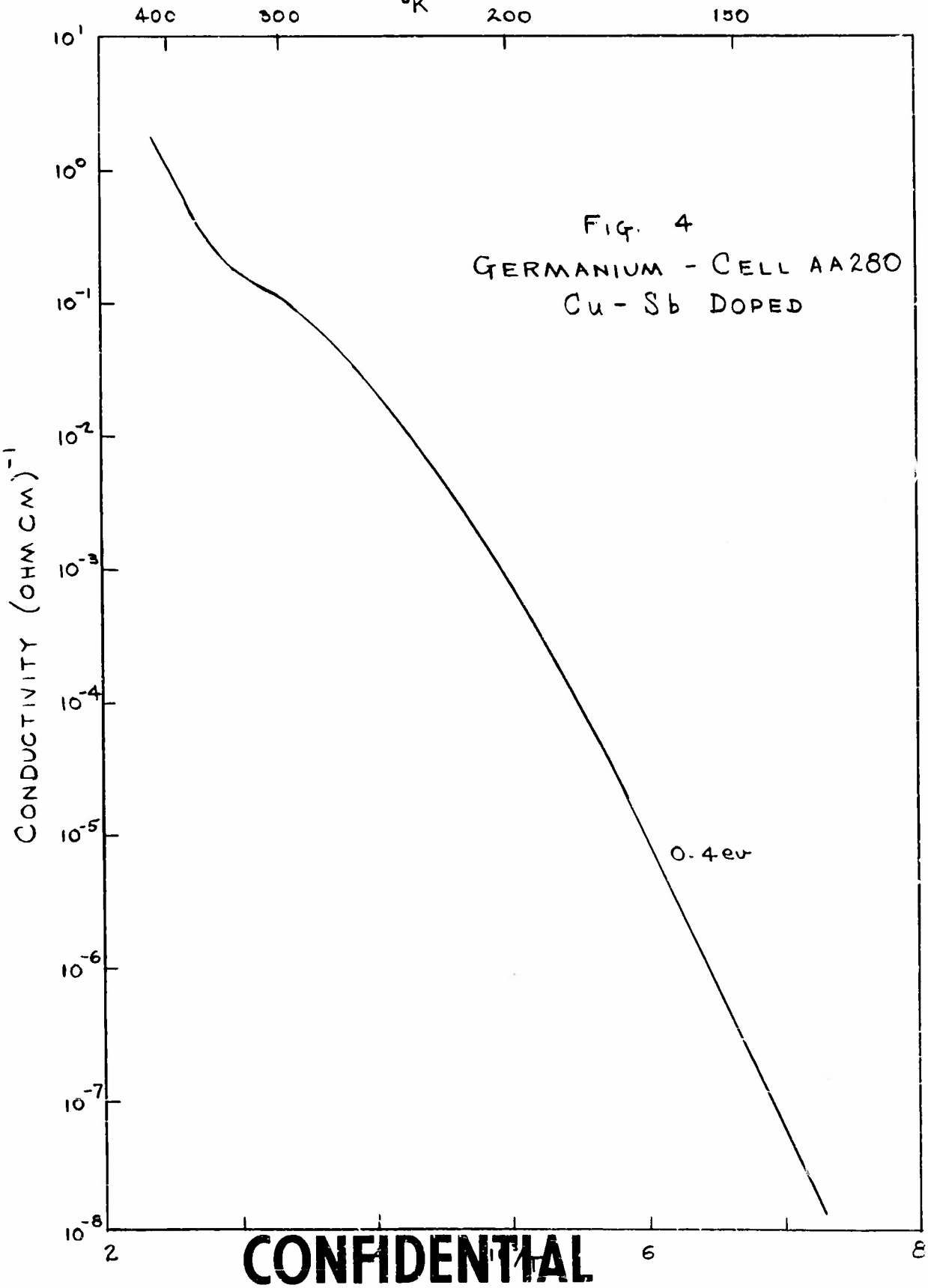


FIG. 4
GERMANIUM - CELL AA280
Cu - Sb DOPED

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